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Preparation of Methylenedifluorocyclopropanes *via* Cyclopropyl Anion Promoted β-Elimination

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Abstract: Preparation of methylenedifluorocyclopropanes **2** through the β-elimination reaction promoted by difluorocyclopropyl anion formed by cleavage of C-Si bond with TBAF is described. Base-catalyzed isomerization of **2** to difluorocyclopropene **11** shows the latter structure thermodynamically more stable in contrast to non-fluorinated cases. Application of this method to the synthesis of methylenedifluorocyclopropylglycine (F_2MCPG) derivative **17** is also presented. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Methylenecyclopropane derivatives (MCPs) are well documented as useful intermediates in synthetic organic chemistry, particularly in ring-opening reactions and cycloadditions with unsaturated compounds.[1-3] In addition, considerable attention has been focused on their biological activities.[4] Biologically active natural substances such as MCPA-CoA or MCPF-CoA having methylenecyclopropane moiety are typical examples.[5,6] These compounds show highly inhibitory activities against general acyl-CoA dehydrogenase or enoyl-CoA hydratase (crotonase), responsible for β-oxidation pathway of fatty acid metabolism.[5,6] Our interest is focused on the modification of such methylenecyclopropanes by introducing fluorine atoms on the ring so that their reactivity would change due to the strong electron-withdrawing nature of fluorine. For example, methylenedifluorocyclopropane (F_2MCP) was shown to act as a reactive Michael acceptor,[7] which would suggest the possibility of F_2MCP to be a useful tool for mechanistic study of enzyme reaction or molecular design of inhibitor of enzyme reaction. In the previous paper,[7,8] we reported the preparation of methylenedifluorocyclopropanes (F_2MCPs) through the elimination reaction of selenoxides derived from difluorocyclopropyl methanol. This method is effective for the preparation of F_2MCPs having alkyl substituent on cyclopropane ring.[9] However, it was found to have a limitation in the case of aryl substituted cyclopropanes due to ring opening rearrangement prior to elimination of selenoxide.[7] Moreover, intramolecular substitution reaction on the selenoxide bearing carbon was also observed as a side reaction in a certain case.[8]

In this paper, we report more efficient method for preparation of F_2MCPs **2** *via* cyclopropyl anion promoted β-elimination reaction using the silylated difluorocyclopropane **1** and tetrabutylammonium fluoride (TBAF).[10] Furthermore, we applied this method to the synthesis of methylenedifluorocyclopropylglycine (F_2MCPG) **3** (Scheme 1).[8]

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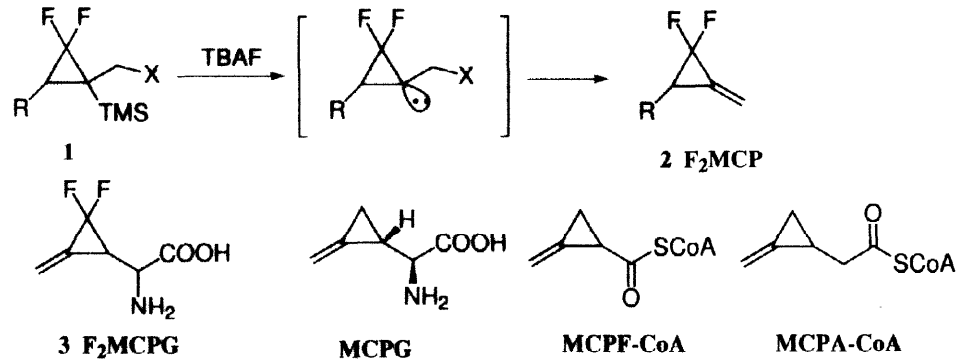
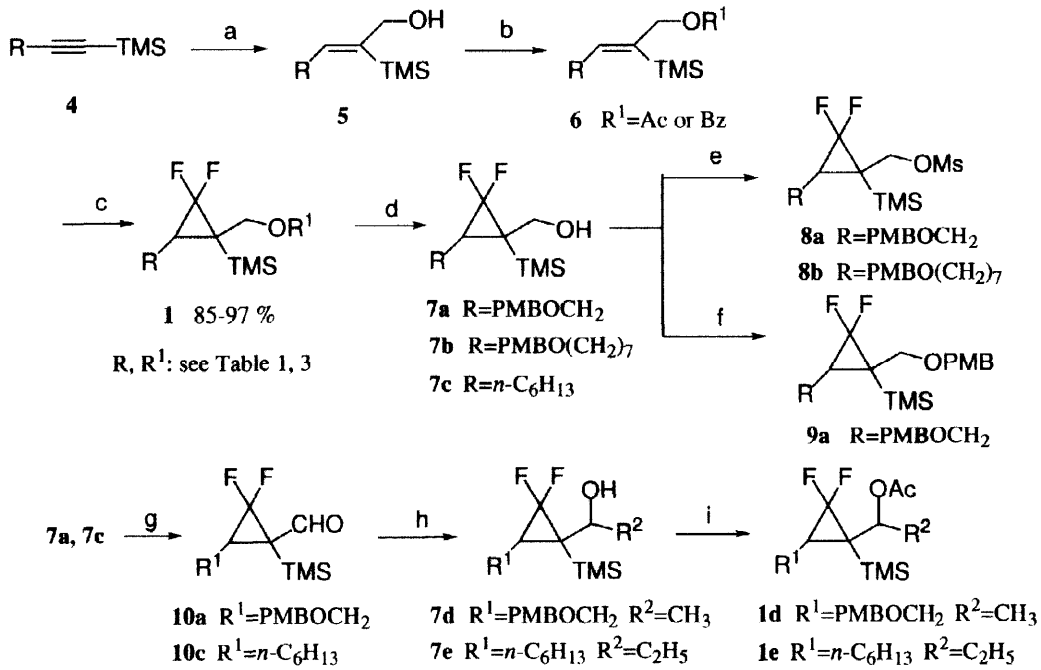
Scheme 1



Results and discussion

The starting trimethylsilylated (*Z*)-allylic alcohol **5** was prepared from the TMS-acetylene **4** according to the reported procedure.[11] Acylation of the hydroxyl group followed by the *cis*-addition of difluorocarbene to the ester gave the difluorocyclopropane **1** (see Table 1, 3) in good yield. While the treatment of the ester **1a-c** with 10% KOH in MeOH at rt or 1% KOH in MeOH under reflux resulted in the protodesilylation predominantly, saponification of **1a-c** with 1% KOH in MeOH at rt gave the alcohol **7a-c** in good yield. The alcohols **7a, 7b** were converted to the mesylate **8a, 8b**. Etherification of **7a** with 4- methoxybenzyl chloride in

Scheme 2



a) DIBAL-H, Et_2O then MeLi, HCHO b) Ac_2O, Py or BzCl, Py c) $ClCF_2COONa$, diglyme, 180 °C
d) 1% KOH, MeOH e) MsCl, Py f) 4-Methoxybenzyl 4-pentenyl ether, NIS
g) ClCOCOCl, DMSO, Et_3N h) R^2MgBr, Et_2O then separation of diastereomer i) Ac_2O, Py

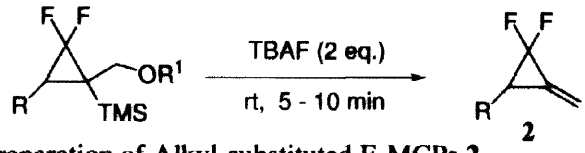


Table 1 Preparation of Alkyl-substituted F_2MCPs **2**

Entry	Substrate	R	R^1	Solvent	2	Yield (%)[a]
1	**1a**	$PMBOCH_2$[b]	Ac	THF	**2a**	66
2	**1a**		Ac	diglyme		68
3	**1a'**		Bz	THF		83
4	**8a**		Ms	diglyme		82
5	**9a**		PMB[b]	THF		0[c]
6	**1b**	$PMBO(CH_2)_7$	Bz	THF	**2b**	91
7	**1b**		Bz	digyme		86
8	**8b**		Ms	diglyme		71
9	**1c**	n-C_6H_{13}	Bz	THF	**2c**	84

a) Isolated yield. b) PMB: 4-methoxybenzyl c) Protodesilylated product, 1,2-bis(4-methoxybenzyloxymethyl)-3,3-difluorocyclopropane, was isolated in 90 % yield.

the presence of NaH was not fruitful giving rise to the protodesilylated compound, but the ether **9a** was obtained under the neutral conditions using 4-methoxybenzyl 4-pentenyl ether and NIS system.[12] Each diastereomer of the acetate form of secondary alcohol **1d** was synthesized as follows; the Swern oxidation of the alcohol **7a** gave the aldehydes **10a**, which reacted with the Grignard reagent to give the alcohol **7d** as a mixture of diastereomers. After separation of the diastereomers by column chromatography, each isomer was acetylated to give less polar-**1d** and more polar-**1d**, respectively. By the similar procedure, less polar-**1e** and more polar-**1e** were obtained (Scheme 2).

We reported that difluorocyclopropyl anion can be easily generated upon treating the trimethylsilylated difluorocyclopropane with TBAF.[10] Thus, it is expected that the methylenation reaction would proceed by β-elimination reaction of the trimethylsilylated difluorocyclopropylmethanol derivatives **1** (or **8**, **9a**). Results with the cyclopropanes having alkyl substituent are summarized in Table 1. Regarding the leaving group, acetate, benzoate and mesylate were found to be effective and the reaction proceeded at rt within 10 min to give the methylenated products **2** in good yields. However, as in the case of **9a**, alkoxyl group didn't work as the leaving group resulting in the formation of only protodesilylated product, 1,2-bis(4-methoxybenzyloxymethyl)-3,3-difluorocyclopropane (Entry 5).

Peterson olefination of hydroxy derivative **7** (treatment of **7** with NaH or KH e.g.) would be an alternative methylenation procedure, which is among the used and convenient methods for the synthesis of alkylidenecyclopropanes without fluorine substituent on the ring.[3,13] However, this did not work well in the case of difluoro derivative **7** due to a facile protodesilylation reaction which would be promoted by a catalytic amount of a base such as NaH and also due to the low reactivity of the silyloxy group as the leaving group.

In the case of secondary alcohol derivatives such as **1d** and **1e**, although relative configurations were not

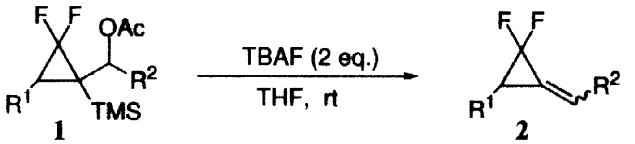


Table 2 Preparation of Alkylidene Difluorocyclopropanes

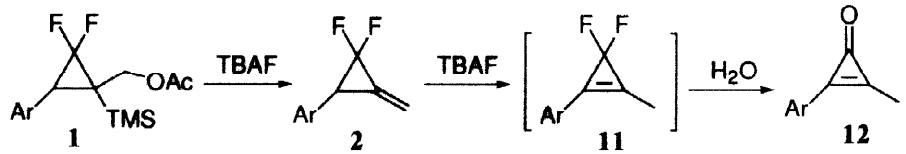
Entry	Substrate[a]	R^1	R^2	2	Yield (%)[b]	*E*/*Z* ratio[c]
1	**1d** less polar	$PMBOCH_2$[d]	Me	**2d**	99	2.7 : 1
2	**1d** more polar				99	1 : 2.2
3	**1e** less polar	*n*-C_6H_{13}	Et	**2e**	60	4 : 1
4	**1e** more polar				52	4 : 3

a) Relative stereochemistry of each diastereomer was not determined. b) Isolated yield. c) Determined by ^{1}H- and ^{19}F-NMR. d) PMB: 4-methoxybenzyl

determined, we examined the stereospecificity of the β-elimination step taking the diastereomerically pure isomers designated as less polar and more polar based on the TLC Rf value. As shown in Table 2, β-elimination step proceeded with a little stereospecificity giving rise to a mixture of *E* and *Z*-isomers of the corresponding alkylidenedifluorocyclopropanes **2d** and **2e**, as long as acetoxy group was used as the leaving group.

In the case of aryl substituted difluorocyclopropanes **1f-1h**, the corresponding F_2MCP **2** and/or the cyclopropenones **12** were obtained by treating with TBAF followed by usual aqueous work-up depending on the reaction conditions and the aryl substituent (Table 3). For example, **1f** (Ar=Ph) gave the F_2MCP **2f** in 80% yield together with the isolation of the cyclopropenone **12f** (5% yield) and the recovery of **1f** (11%) when the reaction was carried out at low temperature (-20 ℃ for 5 min, Entry 1). An exclusive formation of the cyclopropenone **12f** (98% yield) was observed when the reaction was conducted at rt for 2 h (Entry 2). By monitoring the reaction of **1f** with TBAF in THF-$CDCl_3$ by ^{19}F-NMR, the formation of **2f** (-78.0 and -63.1 ppm with geminal coupling 172 Hz) was firstly observed, then the intensity of the additional signal (-46.6 ppm, singlet) possibly due to the cyclopropene **11f**[14] gradually increased. Thus, these results indicate that TBAF acts as a base catalyst for deprotonation and isomerization of **2f** to form the difluorocyclopropene **11f**, which is easily hydrolyzed by aqueous work-up giving rise to the cyclopropenone **12f**.[14] By considering the reaction pathway, the substituent effect of the aryl group on the relationship between the reaction conditions (particularly reaction temperature) and the product distribution can be well understood; that is, electron-donating nature of 4-methoxy group (**1g**, Ar=4-$MeOC_6H_4$) resulted in the retardation of the base-catalyzed isomerization of **2g** (Entries 3-5) as compared with **2f** (Ar=Ph), while electron-withdrawing nature of 4-chloro group (**1h**, Ar=4-ClC_6H_4) enhanced such isomerization observing the formation of the cyclopropenone **12h** even when the reaction was carried out at -78 ℃ (Entries 6-8).

It should be noted that the effect of geminal difluoro substituent on the isomerization between cyclopropene and exomethylene leads to the difluorocyclopropene structure thermodynamically more favorable, while in the cases of non-fluorinated substrates isomerization of alkylcyclopropene to exocyclic double bond compound releasing the strain energy (by 6-10 kcal/mol) is favorable process and such isomerization proceeds



1 2 11 12

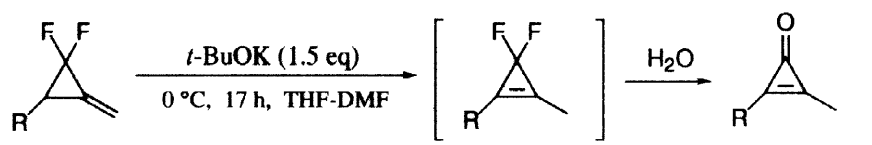
Table 3 Treatment of Aryl-substituted Substrates 1 with TBAF

Entry	Substrate 1	Ar	Temp.	Time	2 (%)[a]	12 (%)[a]	1 (%)[a]
1	**1f**	C_6H_5	-20 °C	5 min	80	5	11
2	**1f**		rt	2 h	-	98	-
3	**1g**	4-$MeOC_6H_4$	-40 ∽ -30 °C	1.5 h	63	2	29
4	**1g**		0 °C	10 min	73	10	-
5	**1g**		rt	20 min	36	58	-
6	**1h**	4-ClC_6H_4	-78 °C	1.5 h	46	25	-
7	**1h**		-40 ∽ -30 °C	1 h	12	39	16
8	**1h**		rt	30 min	-	79	-

a) Isolated yield.

in the presence of *t*-BuOK as the base.[15] For the base catalyzed isomerization of aryl substituted F_2MCP **2f-2h** to the cyclopropene **11f-11h**, TBAF is basic enough as described above, but not for alkyl substituted F_2MCP. Upon treating **2b** with 1.5 eq *t*-BuOK in THF at rt followed by aqueous work-up, the cyclopropenone **12b** was isolated in 75% yield without the recovery of **2b** (Scheme 3). Again, this result suggests that difluorocyclopropene **11** is thermodynamically more stable than methylenedifluorocyclopropane **2** in contrast to non-fluorinated cases. In difluorocyclopropene **11**, the strong electron-withdrawing nature of fluorine makes the fluorine-attached carbon atom positive to stabilize this ring system as 2π-electron aromaticity.

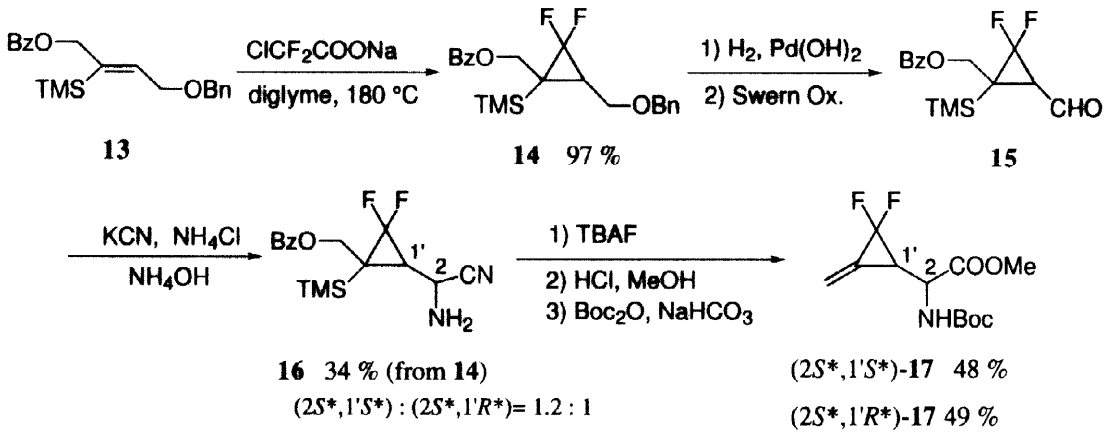
Scheme 3



2b R= $PMBO(CH_2)_7$ **11b** **12b** 75 %

We applied the present method to the preparation of F_2MCPG derivatives **17** (Scheme 4). Trimethylsilylated difluorocyclopropane **14** was obtained by the addition of difluorocarbene to corresponding olefin **13** in good yield. Deprotection of benzyl ether, Swern oxidation followed by the Strecker reaction gave the aminonitrile **16** as a mixture of diastereomers. Each diastereomer separated by column chromatography was treated with TBAF for methylenation and then methanolysis of nitrile group gave the methyl ester. Protection of the amino group with di-*tert*-butyl dicarbonate afforded the desired F_2MCPG derivatives **17**. The relative stereochemistry of the diastereomers was determined by comparing the spectra data with those of the authentic samples.[8]

Scheme 4



In conclusion, F_2MCPs can be prepared by difluorocyclopropyl anion promoted β-elimination using the trimethylsilylated difluorocyclopropane and TBAF, and this was applied to the synthesis of protected F_2MCPGs. Base-catalyzed isomerization of F_2MCPs proceeds to give thermodynamically more stable difluorocyclopropenes, which are easily hydrolysed to the cyclopropenones.

Experimental Section

^{1}H- and ^{13}C-NMR spectra were taken on a Brucker AM400 or a Varian Gemini-300 spectrometer, and chemical shifts were reported in parts per million (ppm) using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H-NMR, and $CDCl_3$ (77.01 ppm) for ^{13}C-NMR as an internal standard, respectively. ^{19}F-NMR spectra were taken on a Brucker AM400 spectrometer, and chemical shifts were reported in parts per million (ppm) using benzotrifluoride as a standard. Infrared spectra (IR) were recorded on a Perkin-Elmer FTIR-1710 infrared spectrophotometer. Mass spectra (MS) were obtained on a Hitachi M-80 or VG Auto spec. Medium pressure liquid chromatography (MPLC) was performed using prepacked column (silica gel, 50 μm) with UV or RI detector.

1-Acetoxymethyl-3,3-difluoro-2-(4-methoxybenzyloxymethyl)-1-trimethylsilylcyclopropane (1a)

Under Ar atmosphere, to a solution of 1-(4-methoxybenzyloxy)-4-acetoxy-3-trimethylsilyl-2-butene (3.56 g, 11.1 mmol) in diglyme (10 ml) was added $ClCF_2COONa$ (16.9 g, 111 mmol) in diglyme (50 ml) dropwise over 8 h at 180-190 ℃. The solution was stirred for 2 h at 180-190 ℃ and poured into ice-cold water after cooling. The mixture was extracted with hexane (3 x 50 ml). The combined organic phases were washed with water (50 ml), dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (hexane/AcOEt=8:1) to obtain 3.9 g (94 %) of **1a** as a colorless oil. IR (neat) ν cm^{-1}; 1745, 1250, 844. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.17 (9 H, s), 1.88 (1 H, ddd, J = 15.3, 7.7, 7.6 Hz), 2.07 (3 H, s), 3.64 (2 H, m), 3.82 (3 H, s), 4.05 (1 H, dd, J = 11.8, 1.3 Hz), 4.23 (1 H, ddd, J = 11.8, 1.9, 1.6 Hz), 4.43 (1 H, d, J = 11.4 Hz), 4.50 (1 H, d, J = 11.4 Hz), 6.90 (2 H, m), 7.27 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ; -0.32, 20.8, 23.6 (dd, J = 18.3, 6.8 Hz), 31.8 (dd, J = 9.8, 9.6 Hz), 55.2, 63.6, 66.0 (d, J

= 9.1 Hz), 72.0, 113.8, 117.3 (dd, J = 293.3, 279.5 Hz), 129.3, 130.1, 159.3, 170.5. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -70.9 (1 F, d, J = 157.0 Hz), -68.9 (1 F, dd, J = 157.0, 15.3 Hz). MS (EI) m/z; 372 (M^+), 312, 121. Anal. Calcd for $C_{18}H_{26}F_2O_4Si$: C, 58.04; H, 7.04. Found: C, 58.29; H, 7.16.

1-Benzoyloxymethyl-3,3-difluoro-2-(4-methoxybenzyloxymethyl)-1-trimethylsilylcyclopropane (1a')

Compound **1a'** was prepared in 83 % yield from 1-(4-methoxybenzyloxy)-4-benzoyloxy-3-trimethylsilyl-2-butene (317 mg, 0.82 mmol). **1a'**: colorless oil. IR (neat) ν cm^{-1}; 1721, 1273, 1251, 844. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.18 (9 H, s), 1.99 (1 H, ddd, J = 13.0, 8.8, 7.8 Hz), 3.63 (1 H, ddd, J = 10.8, 8.8, 1.5 Hz), 3.68 (1 H, ddd, J = 10.8, 7.8, 1.3 Hz), 3.77 (3 H, s), 4.31 (1 H, dd, J = 11.8, 1.6 Hz), 4.40 (1 H, d, J = 11.3 Hz), 4.43 (1 H, dm, J = 11.8 Hz), 4.47 (1 H, d, J = 11.3 Hz), 6.85 (2 H, m), 7.23 (2 H, m), 7.39 (2 H, m), 7.53 (1 H, m), 8.01 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ; -0.27, 23.9 (dd, J = 18.5, 6.8 Hz), 32.0 (dd, J = 9.7, 9.5 Hz), 55.2, 63.7, 66.3 (d, J = 8.3 Hz), 72.0, 113.8, 117.4 (dd, J = 293.7, 279.7 Hz), 128.4, 129.3, 129.6, 129.8, 129.9, 133.0, 159.2, 166.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -70.4 (1 F, d, J = 157.0 Hz), -68.2 (1 F, dd, J = 157.0, 13.0 Hz). MS (EI) m/z; 434 (M^+), 329, 121. Anal. Calcd for $C_{23}H_{28}F_2O_4Si$: C, 63.57; H, 6.49. Found: C, 63.80; H, 6.53.

1-Benzoyloxymethyl-3,3-difluoro-2-[7-(4-methoxybenzyloxy)heptyl]-1-trimethylsilylcyclopropane (1b)

Compound **1b** was prepared in 86 % yield from 1-benzoyloxy-2-trimethylsilyl-10-(4-methoxybenzyloxy)-2-decene (3.78 g, 8.1 mmol). **1b:** colorless oil. IR (neat)ν cm^{-1}; 2940, 2860,1720. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.21 (9 H, s), 0.89 (1 H, dd, J = 7.0, 6.7 Hz), 1.21-1.48 (8 H, m), 1.49-1.72 (4 H, m), 3.43 (2 H, t, J = 6.6 Hz), 3.80 (3 H, s), 4.31 (1 H, dd, J = 11.8, 1.8 Hz), 4.42 (1 H, d, J = 11.8 Hz), 4.43 (2 H, s), 6.88 (2 H, m), 7.26 (2 H, m), 7.45 (2 H, m), 7.57 (1 H, m), 8.04 (2 H, m). ^{13}C- NMR (100.6 MHz, $CDCl_3$)δ; -0.01, 23.7 (dd, J = 17.8, 7.5 Hz), 24.2, 26.0, 28.9, 29.3, 29.5, 29.7, 33.3 (dd, J = 9.6, 9.4 Hz), 55.2, 67.1 (d, J = 8.8 Hz), 70.1, 72.5, 113.7, 118.5 (dd, J = 294.5, 280.3 Hz), 128.4, 129.2, 129.5, 129.9, 130.7, 133.0, 159.1, 166.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -72.0 (1 F, d, J = 154.0 Hz), -68.3 (1 F, dd, J = 154.0, 12.0 Hz). MS (EI) m/z; 518 (M^+), 396, 121. Anal. Calcd for $C_{29}H_{40}F_2O_4Si$: C, 67.15; H, 7.77. Found: C, 67.12; H, 8.04.

1-Benzoyloxymethyl-3,3-difluoro-2-hexyl-1-trimethylsilylcyclopropane (1c)

Compound **1c** was prepared from 1-(4-methoxybenzyloxy)-4-benzoyloxy-3-trimethylsilyl-2-butene (8.0 g, 25.2 mmol). Purification by column chromatography (hexane/AcOEt=50 :1) gave **1c** (9.14 g, 98 %). **1c**: colorless oil. IR ($CHCl_3$) ν cm^{-1};1718, 1606, 1452. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.22 (9H, s), 0.88 (3H, br.t, J =6.8 Hz), 1.22-1.37 (6H, m), 1.37-1.47 (2H, m), 1.53-1.67 (3H, m), 4.32 (1H, dd, J =11.9, 1.9 Hz), 4.42 (1H, d, J =11.8 Hz), 7.42-7.50 (2H, m), 7.58 (1H, br.t, J =7.4 Hz), 8.01-8.06 (2H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 0.00, 14.0, 22.5, 23.8 (dd, J =17.9, 7.7 Hz), 24.3, 28.7, 29.6, 31.7, 33.4 (t, J =9.5 Hz), 67.2 (d, J =8.7 Hz), 118.6 (dd, J =294.5, 280.3 Hz), 128.4, 129.6, 130.0, 133.0, 166.4. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -71.9 (1F, d, J =154 Hz), -68.2 (1F, dd, J =153, 12 Hz). MS(EI) m/z; 368 (M^+), 353 (M^+-CH_3). Calcd for $C_{20}H_{30}O_2F_2Si$: C, 65.18; H, 8.20. Found: C, 65.14; H, 8.29.

1-Acetoxymethyl-3,3-difluoro-2-phenyl-1-trimethylsilylcyclopropane (1f)

Compound **1f** was prepared from 3-acetoxy-1-phenyl-2-trimethylsilylpropene (2.9 g, 11.7 mmol).

Purification by column chromatography (hexane/AcOEt=20 : 1) gave **1f** (2.66 g, 76 %) as a colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1738. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.15 (9H, s), 2.04 (3H, s), 2.85 (1H, d, *J* =14.1 Hz), 4.25 (1H, dd, *J* =11.8, 1.5 Hz), 4.36 (1H, d, *J* =11.8 Hz), 7.24-7.36 (5H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; -1.90, 20.9, 27.6 (dd, *J* =18.3, 6.8 Hz), 35.0 (dd, *J* =12.1, 8.6 Hz), 65.6 (d, *J* =8.9 Hz), 117.4 (dd, *J* =292.7, 282.8 Hz), 127.4, 128.3, 129.7, 132.9, 170.6. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -67.3 (1F, d, *J* =157 Hz), -64.5 (1F, dd, *J* =157, 15 Hz). MS(EI) m/z; 298 (M^+), 221, 166. Anal. Calcd for $C_{15}H_{20}O_2F_2$: C, 60.58; H, 6.76. Found: C, 60.34; H, 6.59.

1-Acetoxymethyl-3,3-difluoro-2-(4-methoxyphenyl)-1-trimethylsilylcyclopropane (1g)

Compound **1g** was prepared from 3-acetoxy-1-(4-methoxyphenyl)-2-trimethylsilylpropene (2.1 g, 7.55 mmol). Purification by column chromatography (hexane/AcOEt=20 :1) gave **1g** (1.67 g, 68 %) as a colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1740, 1614. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.20 (9H, s), 2.17 (3H, s), 2.82 (1H, d, *J* =11.6Hz), 3.73 (1H, dd, *J* =11.9, 1.1 Hz), 3.79 (3H, s), 4.06 (1H, ddd, *J* =11.9, 3.8, 1.3 Hz), 6.83 (2H, m), 7.15 (2H, d, *J* =8.6 Hz). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; -1.84, 20.8, 23.9 (d, *J* =19.5 Hz), 31.4 (t, *J* =10.9 Hz), 55.1, 62.5 (d, *J* =10.9 Hz), 113.9, 116.8 (dd, *J* =289.1, 284.3 Hz), 122.8, 130.8, 158.8, 170.4. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -77.7 (1F, d, *J* =157 Hz), -56.1 (1F, ddd, *J* =157, 12,3 Hz) . MS(EI) m/z; 328 (M^+), 313, 269, 253. Calcd for $C_{16}H_{22}O_3F_2Si$: C, 58.51; H, 6.75. Found: C, 58.44; H, 6.68

1-Acetoxymethyl-3,3-difluoro-2-(4-chlorophenyl)-1-trimethylsilylcyclopropane (1h)

Compound **1h** was prepared from 3-acetoxy-1-(4-chlorophenyl)-2-trimethylsilylpropene (1.93 g, 6.85 mmol). Purification by column chromatography (hexane/AcOEt=30 :1) gave **1h** (1.56 g, 68 %) as a colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1740. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.16 (9H, s), 2.11 (3H, s), 2.77 (1H, d, *J* =13.9 Hz), 4.26 (2H, dd, *J* =38.9, 11.8 Hz), 7.26 (4H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; -1.09, 20.9, 27.8 (dd, *J* =18.0, 6.5 Hz), 34.4 (dd, *J* =12.3, 8.5 Hz), 65.5 (d, *J* =8.7 Hz), 117.1 (dd, *J* =292.2, 282.4 Hz), 128.5, 131.1, 131.6, 133.4, 170.6. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -67.3 (1F, d, *J* =157 Hz), -64.6 (1F, dd, *J* =157, 1 Hz). MS(EI) m/z; 332 (M^+), 272, 270, 257, 255. Calcd for $C_{15}H_{19}O_2F_2SiCl$: C, 54.13; H, 5.75. Found: C, 53.96; H, 5.84.

3,3-Difluoro-1-hydroxymethyl-2-(4-methoxybenzyloxymethyl)-1-trimethylsilylcyclopropane (7a)

A mixture of **1a** (500 mg, 1.34 mmol) and KOH (120 mg, 3 mmol) in MeOH (12 ml) was stirred for 3 h at rt. After evaporation, to the reaction mixture was added water, and then it was extracted with AcOEt. The extracts were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (hexane/AcOEt = 4 : 1) to obtain **7a** (297 mg, 67 %) as a colorless oil. IR (neat) ν cm^{-1}; 3429, 1250, 844. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.18 (9 H, s), 1.81 (1 H, dm, *J* = 4.4 Hz), 2.18 (1 H, brs), 3.57 (1 H, ddt, *J* = 9.5, 8.0, 1.5 Hz), 3.66 (3 H, m), 3.81 (3 H, s), 4.43 (1 H, d, *J* = 11.3 Hz), 4.47 (1 H, d, *J* = 11.3 Hz), 6.89 (2 H, m), 7.27 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ ; -0.20, 27.2 (dd, *J* = 12.9, 10.3 Hz), 31.2 (dd, *J* = 9.7, 9.7 Hz), 55.2, 64.0, 64.6, 72.3, 113.8, 118.0 (dd, *J* = 288.3, 283.9 Hz), 129.6, 129.7, 159.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -69.7 (1 F, d, *J* = 159.0 Hz), -69.5 (1 F, d, *J* = 159.0 Hz). MS (EI) m/z; 330 (M^+), 312, 190. Anal. Calcd for $C_{16}H_{24}F_2O_2Si$: C, 58.16; H, 7.32. Found: C, 57.93; H, 7.24.

3,3-Difluoro-1-hydroxymethyl-2-[7-(4-methoxybenzyloxy)heptyl]-1-trimethylsilylcyclo-

propane (7b)

Compound **7b** was prepared from **1b** (1.04 g, 2.0 mmol). Purification by column chromatography (hexane/AcOEt=7 : 1) gave **7b** (624 mg, 76 %) as a colorless oil. IR (neat) ν cm^{-1}; 3446, 1249, 844. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.19 (9 H, s), 1.20-1.44 (9 H, m), 1.45-1.63 (5 H, m), 3.43 (2 H, t, J = 6.6 Hz), 3.62 (1 H, d, J = 11.6 Hz), 3.73 (1 H, d, J = 11.6 Hz), 3.80 (3 H, s), 4.43 (2 H, s), 6.88 (2 H, m), 7.26 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ ; 0.06, 24.2, 26.1, 27.0 (dd, J = 15.8, 7.9 Hz), 29.0, 29.3, 29.7, 32.2 (dd, J = 9.6, 9.5 Hz), 55.2, 65.4 (d, J = 9.0 Hz), 70.1, 72.5, 113.7, 119.3 (dd, J = 293.0, 281.3 Hz), 129.2, 130.8, 159.1. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ ; -71.4 (1 F, d, J = 154.0 Hz), -69.7 (1 F, ddd, J = 154.0, 13.0, 1.0 Hz). MS (EI) m/z; 414 (M^+), 396, 121. Anal. Calcd for $C_{22}H_{36}F_2O_3Si$: C, 63.73; H, 8.75. Found: C, 63.71; H, 8.79.

3,3-Difluoro-1-(1-hydroxyethyl)-2-(4-methoxybenzyloxy)methyl-1-trimethylsilylcyclopropane (7d)

Under an Ar atmosphere, to a solution of the aldehyde **10a** (791 mg, 2.4 mmol), obtained by treating **7a** with ClCOCOCl, DMSO and Et_3N, in ether (3 ml) was added MeMgBr (2.52 M solution in THF, 1.9 ml, 4.8 mmol) at -70 ℃. The mixture was stirred for 1.5 h at this temperature. The reaction mixture was poured into 10% HCl solution and extracted twice with ether. The combined organic phase was washed with $NaHCO_3$ aq and brine. Then it was dried over Na_2SO_4 and concentrated. The residue was purified by chromatography (hexane/AcOEt=5 : 1) to give less polar-**7d** (529 mg, 64 %) and more polar-**7d** (180 mg, 22 %) in the order of elution. less polar-**7d:** colorless oil. IR ($CHCl_3$) ν cm^{-1}; 3625, 1614. ^{1}H-NMR (400MHz, $CDCl_3$)δ; 0.20 (9H,s), 1.35 (3H, d, J=6.6 Hz), 1.73 (1H, dt, J=13.0, 7.5 Hz), 1.83 1H, d, J=4.0 Hz), 3.63 (2H, d, J=7.5 Hz), 3.69 (1H, m), 3.81 (3H, s), 4.42 (1H, d, J=11.4 Hz), 4.47 (1H, d, J=11.4 Hz), 6.89 (2H, m), 7.26 (2H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 1.65, 21.2, 30.7 (t, J=9.5 Hz), 30.8 (dd, J=7.0, 14.2 Hz), 55.2, 63.8, 71.7 (d, J=9.1 Hz), 72.1, 113.7, 118.4 (dd, J=292.7, 280.3 Hz), 129.3, 129.5, 129.9, 159.2. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -71.0 (1F, dd, J=158, 13 Hz), -68.03 (1F, d, J=157 Hz). MS(EI) m/z; 344(M^+), 309, 281. Anal. Calcd for $C_{17}H_{26}O_3F_2Si$: C, 59.28; H, 7.61. Found: C, 59.05; H, 7.84. more polar-**7d:** colorless oil. IR ($CHCl_3$) ν cm^{-1}; 3624, 1614. ^{1}H-NMR (400MHz, $CDCl_3$)δ; 0.20 (9H, s), 1.34 (3H, d, J=6.6 Hz), 1.79 (1H, s), 1.86 (1H, dt, J=13.1, 7.6 Hz), 3.65 (3H, m), 3.81 (3H, s), 4.44 (1H, d, J=11.4 Hz), 4.47 (1H, d, J=11.4 Hz), 6.88 (2H, m), 7.26 (2H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 1.63, 22.5, 31.8 (dd, J=14.5, 7.3 Hz), 33.7 (t, J=9.2 Hz), 55.2, 60.3, 64.0, 72.3, 73.2 (d, J=5.1 Hz), 113.8, 117.5 (dd, J=293.1, 280.1 Hz), 129.5, 129.7, 159.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -68.2 (1F, dd, J=161.0, 13.0 Hz), -66.9 (1F, d, J=161.0 Hz). MS(EI) m/z; 344(M^+), 309, 281. Anal. Calcd for $C_{17}H_{26}O_3F_2Si$: C, 59.28; H, 7.61. Found: C, 59.50; H, 7.45.

3,3-Difluoro-1-(1-hydroxypropyl)-2-hexyl-1-trimethylsilylcyclopropane (7e)

less polar-**7e:** colorless oil. IR (neat) ν cm^{-1}; 3626, 3477, 1448. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.21 (9 H, s), 0.89 (3H, t, J=7.1 Hz), 0.99 (3H, t, J=7.4 Hz), 1.22-1.44 (9H, m), 1.45-1.75 (5H, m), 3.25 (1H, dm, J=1.7 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ; 2.07, 11.7, 14.0, 22.6, 24.1, 28.8, 29.8, 30.4 (dd, J=13.4, 8.5 Hz), 31.7, 32.3 (dd, J=9.6, 9.5 Hz), 79.3 (d, J=8.8 Hz), 119.7 (dd, J=291.8, 283.3 Hz). ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -70.7 (1 F, dd, J = 154.0, 12.0 Hz), -70.2 (1 F, d, J = 154.0 Hz). MS (EI) m/z; 291 (M^+-1), 275, 201, 177. Anal. Calcd for $C_{15}H_{30}F_2OSi$: C, 61.60; H, 10.34. Found: C, 61.84; H, 10.41.

more polar-**7e**: colorless oil. IR (neat) ν cm^{-1}; 3628, 1446. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.20 (9 H, s), 0.89 (3H, t, *J*=7.0 Hz), 0.97 (3H, t, *J*=7.4 Hz), 1.23-1.70 (13H, m), 3.33 (1H, dm, *J*=3.5 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ; 1.86, 11.1, 14.0, 22.6, 24.2, 28.8, 29.7, 29.9, 31.0 (dd, *J*=14.4, 8.1 Hz), 31.7, 34.5 (t, *J*=9.0 Hz), 79.4 (d, *J*=4.4 Hz), 118.9 (dd, *J*=294.9, 280.9 Hz). ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -68.4 (1 F, d, *J* = 156.0 Hz), -66.9 (1 F, dd, *J* = 156.0 , 14.0 Hz). MS (EI) m/z; 274 (M^+-H_2O), 201, 73. Anal. Calcd for $C_{15}H_{30}F_2OSi$: C, 61.60; H, 10.34. Found: C, 61.46; H, 10.31.

1-(1-Acetoxyethyl)-3,3-difluoro-2-(4-methoxybenzyloxy)methyl-1-trimethylsilylcyclopropane (1d)

After a mixture of less polar-**7d** (100 mg, 0.29 mmol), Ac_2O (0.04 ml, 0.44 mmol), pyridine (0.05 ml, 0.58 mmol) and catalytic amount of DMAP in CH_2Cl_2 (3 ml) was stirred for 50 min at rt, extractive work-up (CH_2Cl_2) followed by column chromatography (hexane/AcOEt=5 : 1) gave less polar-**1d** (107 mg, 95 %) as a colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1732. ^{1}H-NMR (400MHz, $CDCl_3$)δ; 0.21 (9H, s), 1.36 (3H, d, *J*=6.6 Hz), 1.61 (1H, dt, *J*=12.5, 7.5 Hz), 2.04 (3H, s), 3.62 (2H, m), 3.81 (3H, s), 4.42 (1H, d, *J*=11.4 Hz), 4.47 (1H, d, *J*=11.4 Hz), 4.72 (1H, qd, *J*=6.6, 1.3 Hz), 6.88 (2H, m), 7.25 (2H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 1.54, 18.6, 21.2, 28.4 (dd, *J*=16.3, 7.0 Hz), 31.1 (t, *J*=9.8 Hz), 55.2, 63.6, 72.2, 73.2 (d, *J*=9.8 Hz), 113.8, 117.5 (dd, *J*=294.6, 279.0 Hz), 129.6, 129.9, 159.2, 169.5. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -70.8 (1F, dd, *J*=157.0, 12.0 Hz), -69.4 (1F, d, *J*=157.0 Hz). MS(EI) m/z ; 386(M^+), 311, 281. Anal. Calcd for $C_{19}H_{28}O_4F_2Si$: C, 59.04; H, 7.30. Found: C, 58.88; H, 7.06.

Similarly, more polar-**1d** was prepared from more polar-**7d** (191 mg, 0.56 mmol) in 93 % yield. more polar-**1d**: colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1732. ^{1}H-NMR (400MHz, $CDCl_3$)δ; 0.22 (9H, s), 1.38 (3H, d, *J*=6.7 Hz), 2.03 (3H, s), 2.06 (1H, dt, *J*=12.8, 7.7 Hz), 3.62 (2H, m), 3.81(3H, s), 4.41 (1H, d, *J*=11.4 Hz), 4.49 (1H, d, *J*=11.4 Hz), 4.86 (1H, qd, *J*=6.6, 2.4 Hz), 6.89 (2H, m), 7.26 (2H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 1.56, 20.4, 21.2, 29.2 (dd, *J*=16.5, 7.6 Hz), 34.1 (t, *J*=9.2 Hz), 55.1, 63.4, 72.7, 73.4 (d, *J*=4.0 Hz), 113.7, 117.3 (dd, *J*=293.6, 281.0 Hz), 129.1, 130.0, 159.2, 170.1. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -68.3 (1F, d, *J*=160.0 Hz), -67.3 (1F, dd, *J*=160.0 Hz). MS(EI) m/z ; 386 (M^+), 311, 281. Anal. Calcd for $C_{19}H_{28}O_4F_2Si$: C, 59.04; H, 7.30. Found: C, 59.12; H, 7.22.

1-(1-Acetoxypropyl)-3,3-difluoro-2-hexyl-1-trimethylsilylcyclopropane (1e)

less polar-**1e**: colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1732. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.22 (9H, s), 0.89 (3H, t, *J*=7.0 Hz), 0.90 (3H, t, *J*=7.4 Hz), 1.22-1.40 (9H, m), 1.47-1.64 (2H, m), 1.69 (1H, dtd, *J*=14.3, 7.4, 2.0 Hz), 1.78 (1H, dtm, *J*=14.3, 7.5 Hz), 2.05 (3H, s), 4.60 (1H, ddd, *J*=8.9, 5.1, 1.6 Hz). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 1.85, 11.1, 14.0, 21.2, 22.6, 24.0, 27.1, 27.8 (dd, *J* =15.9, 8.1 Hz), 28.8, 29.6, 31.7, 32.4 (dd, *J* =9.8, 9.6 Hz), 78.5 (d, *J* =9.3 Hz), 118.3 (dd, *J* =294.9, 279.5 Hz), 169.8. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -71.5 (1F, d, *J* =154.0 Hz), -69.3 (1F, ddd, *J* =154.0, 14.0, 3.0 Hz). MS(EI) m/z ; 334 (M^+), 319, 305, 275, 43. Anal. Calcd for $C_{17}H_{32}O_2F_2Si$: C, 61.04; H, 9.64. Found: C, 60.99; H, 9.61. more polar-**1e**: colorless oil. IR ($CHCl_3$) ν cm^{-1}; 1744. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.20 (9H, s), 0.86 (3H, t, *J*=7.4 Hz), 0.89 (3H, t, *J*=7.0 Hz), 1.21-1.41 (8H, m), 1.42-1.58 (2H, m), 1.63 (1H, dddd, *J*=14.8, 7.5, 7.3, 3.9 Hz), 1.71 (1H, dddd, *J*=14.6, 8.3, 6.3, 1.5 Hz), 1.79 (1H, dddd, *J*=14.1, 7.5, 7.2, 2.9 Hz), 2.06 (3H, s), 4.56 (1H, ddd, *J*=10.1, 3.5, 3.4 Hz). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 1.97, 10.8, 14.1, 21.1, 22.6, 24.0, 28.1, 28.7, 28.8 (dd, *J* =20.7, 8.4 Hz), 29.6, 31.7, 35.9 (dd, *J* =9.0, 9.2 Hz), 81.6 (d, *J*

=4.6 Hz), 118.5 (dd, J =295.6, 281.2 Hz), 170.7. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -69.6 (1F, d, J =156.0 Hz), -65.8 (1F, dd, J =156.0, 14.0 Hz). MS(EI) m/z; 334 (M^+), 315, 305, 291. HRMS; Calcd for $C_{16}H_{29}O_2F_2Si$ (M^+-CH_3): 319.1905, Found: 319.1931.

3,3-Difluoro-1-mesyloxymethyl-2-(4-methoxybenzyloxymethyl)-1-trimethylsilylcyclopropane (8a)

After a mixture of **7a** (565 mg, 1.71 mmol), pyridine (349 mg, 4.42 mmol) and MsCl (460 mg, 4.01 mmol) in CH_2Cl_2 (5 ml) was stirred for 4 h at 0 ℃, extractive work-up (CH_2Cl_2) gave the crude mesylate **8a**, which was used in the next step without further purification.

General procedure for the preparation of alkyl substituted methylenecyclopropanes (2)

To a solution of **1** (0.40 mmol) in solvent (4 ml) (see Table 1) was added TBAF (1 M in THF, 0.8 ml, 0.8 mmol), and then the reaction mixture was stirred for 5 min-1 h at rt. The mixture was poured into water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography.

3,3-Difluoro-2-(4-methoxybenzyloxymethyl)methylenecyclopropane (2a)

Compound **2a** was prepared from **1a** (150 mg, 0.40 mmol) in THF. Purification by column chromatography (hexane/AcOEt = 8 : 1) gave **2a** (63 mg, 66 %) as a colorless oil. IR (neat) ν cm^{-1}; 2865, 1514, 1250, 1173. ^{1}H-NMR (400 MHz, $CDCl_3$)δ ; 2.53 (1 H, m), 3.54 (1 H, ddd, J = 10.8, 8.4, 1.9 Hz), 3.64 (1 H, dddd, J = 10.8, 6.3, 3.4, 1.3 Hz), 3.81 (3 H, s), 4.46 (1 H, d, J = 11.5 Hz), 4.53 (1 H, d, J = 11.5 Hz), 5.74 (1 H, dd, J = 4.5, 2.3 Hz), 6.04 (1 H, ddm, J = 1.7, 1.7 Hz), 6.90 (2 H, m), 7.29 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ ; 29.3 (dd, J = 12.4, 12.3 Hz), 55.2, 65.3, 72.3, 107.0 (dd, J = 291.6, 291.6 Hz), 112.7, 113.8, 129.3, 129.7 (dd, J = 7.5, 7.3 Hz), 129.9, 159.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ; -78.0 (1 F, d, J = 179.0 Hz), -65.2 (1 F, dd, J = 179.0, 10.0 Hz). MS (EI) m/z; 240 (M^+), 136, 121. Anal. Calcd for $C_{13}H_{14}F_2O_2$: C, 64.99; H, 5.87. Found: C, 64.85; H, 6.01.

3,3-Difluoro-2-[7-(4-methoxybenzyloxy)heptyl]methylenecyclopropane (2b)

Compound **2b** was prepared from **1b** (100 mg, 0.19 mmol) in THF. Purification by column chromatography (hexane/AcOEt = 8 : 1) gave **2b** (56 mg, 91 %) as a colorless oil. IR (neat) ν cm^{-1}; 2934, 1513, 1249, 1173. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 1.33-1.70 (12 H, m), 2.15 (1 H, dm, J = 3.3 Hz), 3.50 (2 H, t, J = 6.6 Hz), 3.85 (3 H, s), 4.49 (2 H, s), 5.68 (1 H, dd, J = 4.6, 2.4 Hz), 5.99 (1 H, dm, J = 1.6 Hz), 6.94 (2 H, m), 7.32 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ ; 25.9, 26.1, 28.6, 28.9, 29.2, 29.3 (t, J = 12.8 Hz), 29.7, 55.2, 70.1, 72.5, 108.1 (dd, J = 292.5, 292.3 Hz), 110.6, 113.7, 129.2, 130.7, 133.2 (dd, J = 7.0, 6.9 Hz), 159.1. ^{19}F-NMR (376.5 MHz, $CDCl_3$)δ ; -79.8 (1 F, d, J = 176.0 Hz), -64.8 (1 F, dd, J = 176.0, 12.0 Hz). MS (EI) m/z; 324 (M^+), 302, 191. Anal. Calcd for $C_{19}H_{26}F_2O_2$: C, 70.35; H, 8.08. Found: C, 70.18; H, 8.13.

3,3-Difluoro-2-hexyl-methylenecyclopropane (2c)

Compound **2c** was prepared from **1c** (2.11 g, 6.0 mmol). Purification by column chromatography (hexane/AcOEt = 40 : 1) gave **2c** (872 mg, 84 %) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.89 (3H, br.t, J=6.8 Hz), 1.25-1.38 (6H, m), 1.38-1.48 (2H, m), 1.48-1.62 (2H, m), 2.04-2.15 (1H, m), 5.63 (1H, dd, J=4.6, 2.4 Hz), 5.94 (1H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 14.1, 22.6, 26.0, 28.8 (d, J =7.38 Hz), 29.4 (dd, J =13.4, 10.8 Hz), 31.7, 108.2 (t, J =292.5 Hz), 110.6, 133.4 (t, J =6.8 Hz). ^{19}F-NMR (376.5

MHz, $CDCl_3$) δ ;-79.8 (1F, d. *J*=176 Hz), -64.8 (1F, dd, *J*=176, 12 Hz). MS(EI) m/z ; 174 (M^+), 159, 104. HRMS; Calcd for $C_9H_{13}F_2$ (M^+-CH_3): 159.0985, Found: 159.0984.

3,3-Difluoro-2-(4-methoxybenzyloxy)methyl-1-methylidenecyclopropane (2d)

Compound **2d** was prepared from less polar-**1d** (104 mg, 0.27 mmol). Purification by column chromatography (hexane/AcOEt = 5 : 1) gave **2d** (68 mg, 99 %) as a mixture of stereoisomers (*E* /*Z* =2.7 : 1). The mixture was separated by MPLC (hexane /AcOEt = 10 : 1). less polar-**2d:** colorless oil. IR (neat) ν cm^{-1}; 1770, 1614. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 1.90 (3H, ddd, *J*=12.1, 6.8, 2.6 Hz), 2.45 (1H, m), 3.51 (1H, ddd, *J*=10.5, 8.2, 1.8 Hz), 3.66 (1H, dddd, *J*=10.5, 6.3, 3.4, 1.1 Hz), 3.81 (3H, s), 4.45 (1H, d, *J*=11.5 Hz), 4.53 (1H, d, *J*=11.5 Hz), 6.49 (1H, qd, *J*=6.8, 3.2 Hz), 6.89 (2H, m), 7.28 (2H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 16.9, 28.7 (t, *J*=12.5 Hz), 55.2, 65.6 (d, *J*=2.8 Hz), 72.3, 107.6 (t, *J*=290.1 Hz), 113.8, 121.4 (t, *J*=7.6 Hz), 125.2, 129.2, 130.1, 159.2. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -78.6 (1F, d, *J*=174 Hz), -63.6 (1F, dm, *J*=174 Hz). MS(EI) m/z; 254 (M^+), 224, 209. Anal. Calcd for $C_{14}H_{16}F_2O_2$: C, 66.13; H, 6.34. Found: C, 66.00; H, 6.41. more polar-**2d:** colorless oil. IR (neat) ν cm^{-1}; 1770, 1614. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 1.95 (3H, m), 2.48 (1H, m), 3.51 (1H, ddd, *J*=10.5, 8.3, 1.8 Hz), 3.61 (1H, dddd, *J*=10.5, 6.0, 3.4, 1.3 Hz), 3.81 (3H, s), 4.46 (1H, d, *J*=11.5 Hz), 4.52 (1H, d, *J*=11.5 Hz), 6.10 (1H, m), 6.91 (2H, m), 7.28 (2H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 18.3, 29.3 (t, *J*=12.4 Hz), 55.1, 65.7 (d, *J*=2.4 Hz), 72.1, 107.8 (t, *J*=290.6 Hz), 113.8, 120.9 (t, *J*=6.3 Hz), 125.7, 129.2, 130.0, 159.2. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -77.9 (1F, d, *J*=176.0 Hz), -64.9 (1F, dd, *J*=176.0, 9.0 Hz). MS(EI) m/z; 254(M^+), 224, 209. Anal. Calcd for $C_{14}H_{16}F_2O_2$: C, 66.13; H, 6.34. Found: C, 65.84; H, 6.37.

3,3-Difluoro-2-hexyl-1-propylidenecyclopropane (2e)

less polar-**2e:** colorless oil. IR (neat) ν cm^{-1}; 1762. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.89 (3H, t, *J* =6.7 Hz), 1.11 (3H, t, *J*=7.4 Hz), 1.21-1.36 (6H, m), 1.37-1.58 (4H, m), 2.02 (1H, m), 2.25 (2H, dm, *J*=3.0 Hz), 6.10 (1H, dddm, *J*=8.0, 5.3, 2.6 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 11.8, 14.1, 22.6, 25.5, 26.4 (d, *J*=3.1 Hz), 28.7 (t, *J*=13.4 Hz), 28.8, 31.7, 108.8 (dd, *J*=292.1, 291.6 Hz), 122.6 (dd, *J*=6.8, 6.0 Hz), 130.1. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -76.3 (1F, d, *J* =171.7 Hz), -61.6 (1F, dd, *J*=171.7, 10.8 Hz). MS(EI) m/z; 187 (M^+-CH_3), 173, 159. HRMS; Calcd for $C_{12}H_{20}F_2$ (M^+): 202.1533, Found: 202.1530. more polar-**2e:** colorless oil. IR (neat) ν cm^{-1}; 1762. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 0.89 (3H, t, *J* =7.0 Hz), 1.08 (3H, t, *J*=7.5 Hz), 1.22-1.38 (6H, m), 2.07 (1H, m), 2.24 (2H, ddm, *J*=5.0, 2.3 Hz), 6.39 (1H, td, *J*=6.7, 3.1 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 13.1, 14.1, 22.6, 24.7, 26.8 (d, *J*=3.1 Hz), 28.9, 29.0 (dd, *J*=12.8, 11.0 Hz), 29.2, 31.7, 108.5 (dd, *J*=290.5, 290.4 Hz), 123.0 (dd, *J*= 6.9, 6.7 Hz), 129.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -78.9 (1F, dd, *J* =171.1, 1.8 Hz), -63.6 (1F, ddm, 171.7, 10.3 Hz). MS(EI) m/z; 187 (M^+-CH_3), 173, 159. HRMS; Calcd for $C_{12}H_{20}F_2$ (M^+): 202.1533, Found: 202.1531.

3,3-Difluoro-2-phenylmethylenecyclopropane (2f) and 2-Methyl-3-phenylcyclopropenone (12f)

After stirring a mixture of **1f** (120 mg, 0.4 mmol) and TBAF (1 M in THF, 0.8 ml, 0.8 mmol) in THF (2 ml) at -20 ℃ for 5 min (Table 3, Entry 1), the mixture was poured into water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (hexane/AcOEt=10 : 1, then AcOEt) to give **2f** (53 mg, 80 %), **12f** (3 mg, 5 %) and the recovery of **1f** (13 mg, 11 %). **2f:** colorless oil. IR (neat) ν cm^{-1}; 3028, 1862, 1736. ^{1}H-NMR (400 MHz,

$CDCl_3$)δ; 3.31 (1H, ddd, J =3.5, 7.1, 10.3 Hz), 5.87-5.91 (1H, m), 6.17-6.21 (1H, m), 7.13-7.18 (2H, m), 7.19-7.30 (3H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 34.2 (t, J =12.7 Hz), 106.1 (dd, J =292.3, 297.2 Hz), 114.0, 127.4, 128.3, 128.5, 130.8 (t, J =7 Hz), 132.0 (d, J =2.9 Hz). ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -78.0 (1F, dd, J =172.4, 3.8 Hz), - 63.1 (1F, dd, 172.4, 10.2 Hz). MS(EI) m/z; 166 (M^+), 151, 146. HRMS; Calcd for $C_{10}H_8F_2$ (M^+): 166.059407, Found: 166.058923. **12f:** colorless crystals. mp.68-69.5 ℃ (from hexane-AcOEt). IR ($CHCl_3$) ν cm^{-1}; 3008, 1856, 1630. ^{1}H-NMR (300 MHz, $CDCl_3$)δ; 2.49 (3H, s), 7.45-7.60 (2H, m), 7.74-7.82 (2H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 11.4, 123.5, 129.0, 130.8, 132.3, 151.5, 154.5, 156.5. MS(EI) m/z ; 145 (M^++1), 115. Anal. Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.07; H, 5.63.

3,3-Difluoro-2-(4-methoxyphenyl)methylenecyclopropane (2g) and 2-Methyl-3-(4-methoxyphenyl)cyclopropenone (12g)

To a solution of **1g** (328 mg, 1.0 mmol) in THF (2 ml) was added TBAF (1 M in THF, 2.0 ml, 2.0 mmol) at 0 ℃, and then the reaction mixture was stirred for 10 min at the same temperature (Table 3, Entry 4). The mixture was poured into water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (hexane/AcOEt =10 : 1 then AcOEt) to give **2g** (143 mg, 73 %) and **12g** (18 mg, 10 %) in the order of elution. **2g**: colorless oil: IR ($CHCl_3$) ν cm^{-1}; 3032, 2968, 2940, 2912, 2836, 1763, 1614. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 3.34 (1H, ddd, J =10.2, 6.9, 3.3 Hz), 3.80 (3H, s), 5.94 (1H, d, J =3.1 Hz), 6.24 (1H, d, J =3.1 Hz), 6.87 (2H, d, J =8.5 Hz), 7.15 (2H, d, J =8.6 Hz). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 33.4 (t, J =12.6 Hz), 55.2, 106.1 (dd, J =296.7, 291.8 Hz), 113.8, 123.8 (d, J =3.1 Hz), 129.4, 131.2 (t, J =6.8 Hz), 159.0. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -78.2 (1F, d, J =172 Hz), -63.6 (1F, dd, J =173, 10 Hz). MS(EI) m/z ; 196 (M^+), 181, 176, 165. HRMS; Calcd for $C_{11}H_{10}OF_2$ (M^+): 196.0700, Found: 196.0701. **12g**: colorless crystals. mp 102-103 ℃. IR ($CHCl_3$) ν cm^{-1}; 3004, 1858, 1734, 1622, 1604. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 2.42 (3H ,s), 3.87 (3H, s), 6.99 (2H, m), 7.72 (2H, m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 11.0, 55.2, 114.4, 116.3, 132.9, 147.3, 153.6, 156.2, 162.5. MS(EI) m/z; 175 (M^++1), 159, 146, 131. HRMS; Calcd for $C_{10}H_{10}O$ (M^+-CO): 146.0732, Found: 146.0761

2-(4-Chlorophenyl)-3,3-difluoro-methylenecyclopropane (2h) and 2-(4-chlorophenyl)-3-methylcyclopropenone (12h)

Compounds **2h** and **12h** was prepared from **1h** (390 mg, 1.17 mmol) at -70 ℃ (Table 3, Entry 6). The products were purified by column chromatography (hexane/AcOEt =50 : 1 then AcOEt) to give **2h** (109 mg, 46 %) and **12h** (46 mg, 25 %) in the order of elution. **2h**: colorless oil. IR ($CHCl_3$) ν cm^{-1}; 3040, 1764, 1490. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 3034 (1H, m), 5.97 (1H, d, J=3.1 Hz), 6.28(1H, d, J=3.1 Hz), 7.15 (2H, d, J=8.3 Hz), 7.30 (2H, d, J=8.3 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 33.4 (t, J =12.9 Hz), 105.8 (dd, J =292.0, 297.3 Hz), 114.5, 128.7, 129.6, 130.5 (t, J =7.1 Hz), 130.6 (d, J =3.2 Hz), 133.4. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ ; -77.8 (1F, d, J=172 Hz), -63.2 (1F, dd, J=172, 10 Hz). MS(EI) m/z; 200, 165. HRMS Calcd for $C_{10}H_7ClF_2$ (M^+): 200.0204, Found: 200.0202. **12h:** colorless crystals. mp 116-117 ℃. IR ($CHCl_3$) ν cm^{-1}; 3020, 1858, 1634. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 2.49 (3H, s), 7.51 (2H, m), 7.71 (2H,m). ^{13}C-NMR (75.2 MHz, $CDCl_3$) δ ; 11.5, 121.9, 129.5, 132.0, 138.6, 151.9, 153.4, 156.1. MS(EI) m/z; 179 (M^+), 152. Calcd for $C_{10}H_7ClO$: C, 67.24; H, 3.95. Found: C, 67.00; H, 4.21.

2-Methyl-3-(4-methoxybenzyloxyheptyl)cylopropenone (12b)

Under argon atmosphere to a suspension of KOBu^t (57 mg, 0.51 mmol) in THF (3 ml) was added **2b** (110 mg, 0.34 mmol) in THF-DMF (5 ml-2.5 ml) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 17 h. The mixture was poured into NH_4Cl solution and extracted with ether twice. The extracts were washed with brine, dried over Na_2SO_4 and evaporated to dryness. Purification by column chromatography (hexane/AcOEt = 1 : 3) gave **12b** (88 mg, 75 %) as a colorless oil. IR ($CHCl_3$) ν cm^{-1}; 3000, 1850, 1616. ^{1}H-NMR (400 MHz, $CDCl_3$)δ; 1.28-1.42 (6H, m), 1.54-1.62 (2H, m), 1.63-1.72 (2H, m), 2.23 (3H, s), 2.56 (2H, t, J=7.3 Hz), 3.42 (2H, t, J=6.5 Hz), 3.78 (3H, s), 4.41 (2H, s), 6.86 (2H, d, J=8.9 Hz), 7.24 (2H, d, J=8.5 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ ; 11.2, 25.96, 26.0, 26.2, 28.9, 29.1, 29.6, 55.2, 70.0, 72.5, 113.7, 129.2, 130.7, 156.9, 159.1, 159.7, 161.5.

1-Benzoyloxymethyl-2-benzyloxymethyl-3,3-difluoro-1-trimethylsilylcyclopropane (14)

Similarly to the preparation of **1a**, addition of difluorocarbene to the TMS-olefin **13** gave **14** as a colorless oil. IR (neat) ν cm^{-1}; 2958, 1722, 1273, 843. ^{1}H-NMR (400 MHz, $CDCl_3$) δ; 0.23 (9 H, s), 2.06 (1 H, ddd, J = 13.0, 7.8, 7.7 Hz), 3.73 (2 H, m), 4.37 (1 H, dd, J = 11.8, 1.7 Hz), 4.49 (1 H, d, J = 11.8 Hz), 4.53 (1 H, d, J = 11.6 Hz), 4.59 (1 H, d, J = 11.6 Hz), 7.26-7.38 (5 H, m), 7.43 (2 H, m), 7.57 (1 H, m), 8.06 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$)δ; -0.29, 24.0 (dd, J = 18.6, 6.9 Hz), 32.0 (dd, J = 9.7, 9.6 Hz), 64.0, 66.3 (d, J = 8.3 Hz), 72.4, 117.5 (dd, J = 293.8, 279.6 Hz), 127.6, 127.7, 128.4, 128.4, 129.6, 133.1, 137.8, 166.3. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ; -70.3 (1 F, d, J = 157.0 Hz), -68.2 (1 F, dd, J = 157.0, 13.0 Hz). MS (EI) m/z; 404 (M^+), 313, 105, 91. Anal. Calcd for $C_{22}H_{26}F_2O_3Si$: C, 65.32; H, 6.48. Found: C, 65.53; H, 6.55.

(2*S,1'*S**) and (2*S**,1'*R**)-2-Amino-2-(2-benzoyloxymethyl-3,3-difluoro-2-trimethylsilyl-cyclopropyl)acetonitrile (16)**

Under hydrogen atmosphere a mixture of **14** (7.8 g, 19.4 mmol) and $Pd(OH)_2$ in AcOEt (10 ml) was stirred for 12 h at rt. The reaction mixture was passed through silica-gel pad to remove insoluble material by washing with AcOEt to give the crude alcohol (5.8 g, 97 %) after evaporation of solvent. Under argon atmosphere to a mixture of oxalyl chloride (0.28 ml, 3.2 mmol) and DMSO (0.45 ml, 6.4 mmol) in CH_2Cl_2 (10 ml) was added a solution of the crude alcohol (904 mg, 2.1 mmol) in CH_2Cl_2 (6 ml) at -78 ℃ and the mixture was stirred for 45 min, then this was traeted with triethylamine (2.0 ml, 14.6 mmol) for 15 min at -78 ℃ and for another 15 min at rt. The reaction mixture was poured into water and extracted with ether (30 ml x 2). The organic extracts were washed with brine, dried over $MgSO_4$ and concentrated to give the crude aldehyde **15** (880 mg, 97 %). A mixture of the crude aldehyde (848 mg, 2.6 mmol), KCN (172 mg, 2.1 mmol) and NH_4Cl (155 mg, 2.9 mmol) in Et_2O (10 ml), 30 %NH_4OH (0.5 ml) and water (1.2 ml) was stirred for 6 h at rt. After addition of sat.$NaHCO_3$ solution, the reaction mixture was extracted with AcOEt and the organic extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed (hexane/AcOEt = 10 : 1 - 4 : 1) to give (2*S**,1'*S**)-**16** (163 mg, 18 %) and (2*S**,1'*R**)-**16** (140 mg, 16 %), respectively. **(2*S**,1'*S**)-16:** colorless oil. IR (neat) ν cm^{-1}; 1719, 1275, 846. ^{1}H-NMR (400 MHz, $CDCl_3$) δ; 0.26 (9 H, s), 1.78 (2 H, brs), 2.11 (1 H, dd, J = 11.0, 10.8 Hz), 3.64 (1 H, d, J = 10.8 Hz), 4.34 (1 H, dd, J = 12.0, 1.6 Hz), 4.44 (1 H, dm, J = 12.0 Hz), 7.46 (2 H, m), 7.58 (1 H, m), 8.03 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ; -0.47, 25.2 (dd, J = 18.5, 6.5 Hz), 35.9 (dd, J = 10.0, 9.7 Hz), 38.5 (d, J = 3.5 Hz), 65.2 (d, J = 7.5 Hz),

115.7 (dd, J = 296.9, 278.3 Hz), 120.6, 128.5, 129.6, 133.3, 166.2. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ; -71.0 (1 F, d, J = 161.0 Hz), -68.7 (1 F, dd, J = 161.0, 11.0 Hz). MS (EI) m/z; 339 (M^+), 323, 312, 105. Anal. Calcd for $C_{16}H_{20}F_2N_2O_2Si$: C, 56.78; H, 5.96; N, 8.28. Found: C, 56.80; H, 6.01; N, 8.22. **(2*S**,1'*R**)-16**: colorless oil. IR (neat) ν cm^{-1}; 1720, 1274, 846. ^{1}H-NMR (400 MHz, $CDCl_3$) δ; 0.29 (9 H, s), 1.86 (2 H, brs), 2.06 (1 H, dd, J = 12.0, 10.7 Hz), 3.79 (1 H, d, J = 10.7 Hz), 4.36 (1 H, dm, J = 12.0 Hz), 4.41 (1 H, dd, J = 12.0, 2.0 Hz), 7.44 (2 H, m), 7.56 (1 H, m), 8.08 (2 H, m). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ; -0.34, 25.1 (dd, J = 19.0, 6.6 Hz), 36.7 (dd, J = 10.0, 9.8 Hz), 40.4 (d, J = 3.9 Hz), 64.8 (d, J = 7.1 Hz), 116.1 (dd, J = 297.5, 277.9 Hz), 120.4 (d, J = 3.6 Hz), 128.5, 129.3, 129.7, 133.3, 166.2. ^{19}F- NMR (376.5 MHz, $CDCl_3$) δ; -73.1 (1 F, d, J = 160.0 Hz), -68.9 (1 F, dd, J = 160.0, 12.0 Hz). MS (EI) m/z; 338 (M^+), 323, 105, 77. Anal. Calcd for $C_{16}H_{20}F_2N_2O_2Si$: C, 56.78; H, 5.96; N, 8.28. Found: C, 56.75; H, 6.20; N, 8.13.

Methyl (2*S,1'*S**)-*N*-Boc-2-(3,3-difluoro-2-methylenecyclopropyl)glycinate [(2*S**,1'*S**)-17]**

After a mixture of (2*S**,1'*S**)-**16** (57 mg, 0.17 mmol) and TBAF (1 M in THF, 0.17 ml) in THF (3 ml) was stirred at rt for 15 min, sat. NaCl solution was added and the mixture was extracted with AcOEt. The organic extract was dried over $MgSO_4$ and concentrated to leave a residue, which was dissolved in MeOH (4 ml) containing AcCl (0.12 ml) and the whole was stiirred at rt for 12 h. After concentrated under reduced pressure, the residue was treated with $NaHCO_3$ (141 mg, 1.7 mmol) and di-*tert*-butyl dicarbonate (55 mg, 0.25 mmol) in a mixture of dioxane (3 ml) and water (1 ml) at rt for 3 h. Extractive work-up (AcOEt) followed by purification by column chromatography (hexane/AcOEt=8 : 1) gave (2*S**,1'*S**)-**17** (22 mg, 48 %) as colorlesss crystals. mp 49.5-50.5 ℃. IR (KBr) ν cm^{-1}; 3361, 1744, 1681, 1523, 1162. ^{1}H-NMR (400 MHz, $CDCl_3$) δ; 1.44 (9 H, s), 2.56 (1 H, m), 3.78 (3 H, S), 4.30 (1 H, brs), 5.21 (1 H, brs), 5.80 (1 H, s), 6.10 (1 H, d, J = 3.2 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ; 28.2, 30.8 (t, J = 12.4 Hz), 50.6, 52.8, 80.4, 105.8 (dd, J = 291.7, 293.9 Hz), 114.1, 128.3(t, J = 7.6 Hz), 154.9, 170.7. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ; -64.4 (1 F, d, J = 179.5 Hz), -75.5 (1 F, d, J = 179.5 Hz). MS(CI) m/z; 278(M^++1), 260, 222, 216, 178. Anal. Calcd for $C_{12}H_{17}F_2NO_4$: C, 51.98; H, 6.18; N, 5.05. Found: C, 52.21; H, 6.30; N, 4.73.

Methyl (2*S,1'*R**)-*N*-Boc-2-(3,3-difluoro-2-methylenecyclopropyl)glycinate [(2*S**,1'*R**)-17]**

(2*S, 1'*R**)-17:** colorless crystals. mp 67.5-68.8 ℃. IR (KBr) ν cm^{-1}; 3365, 1730, 1680, 1518. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.42 (9 H, s), 2.56 (1 H, brs), 3.78 (3 H, s), 4.28 (1 H, brs), 5.19 (1 H, d, J = 7.9 Hz), 5.80 (1 H, s), 6.09 (1 H, d, J = 3.2 Hz). ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ; 28.2, 30.4 (t, J = 12.3 Hz), 50.8, 52.7, 80.3, 105.9 (t, J = 294.0, 291.2 Hz), 114.7, 127.8 (t, J = 7.5 Hz), 154.8, 170.8. ^{19}F-NMR (376.5 MHz, $CDCl_3$) δ; -64.7 (1 F, d, J = 180.6 Hz), -75.5 (1 F, d, J = 180.6 Hz). MS(EI) m/z; 278 (M^++1), 262, 221, 204, 178, 162, 158, 133, 118, 98, 57. Anal. Calcd for $C_{12}H_{17}F_2NO_4$: C, 51.98; H, 6.18; N, 5.05. Found: C, 52.12; H, 6.36; N, 4.76.

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